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Improvements on Pozzolanic Reactivity of Coal Refuse by Thermal Activation

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Abstract

Today, coal refuse as industrial solid waste stockpiled on the ground is one of the greatest threats to the environment. One of the practical solutions to utilize this huge amount of solid waste is to activate the coal refuse and utilize it as substitution for portion of ordinary Portland cement. The key purpose of activation is to enhance the pozzolanic property of the coal refuse.Many scientists and engineers found that thermal activation is a practical approach on increasing pozzolanic property. For thermal activation, temperature and time are two important parameters which significantly determine the activation effect. In this paper, a systematic research has been conducted to seek for anoptimal solution for enhancing pozzolanic reactivity of the relatively inert solid waste-coal refuse in order to improve the utilization efficiency and economy benefit forconstruction and building materials.The mechanical property analysis shows that coal refusethat activated at 700°C to 800°C with 1 hour to 1.5 hours has much higher reactivity when compared with coal refuse activated at 500°C to 600 °C with 1 hour to 1.5 hours. And 28-dayscompressive strength value of prepared blended cementitious material containing 25% of the 700°C 1h activated coal refuse based pozzolanareaches 43.4MPa, which is higher than 28-days strength of OPC group as control.

Keywords: coal refuse, thermal activation, cementitious material, pozzolanic property

1. Introduction

Today, coal is still considered as the primary fuel for electricity generation (CTAB, 2010). However, the coal mining industry also generates a huge amount of inert solid waste during the mining process. And coal refuse is one of the largest forms of waste from the coal mining industry and is generally defined as a low BTU-value material under the parameters of minimum ash content combined with maximum heating value (US EPA, 2008). It is estimated that coal mines in the US generate 109 million metric tons (120 million short tons) of coal refuse from 600 coal preparation plants in 21 coal-producing states annually. In China, the accumulative stockpile of coal refuse has reached 3.8 billion metric tons and it is estimated that over 200 million metric tons of this waste is impounded annually. Therefore, at present, such large quantities of the solid waste have not only occupied a great amount of land but also caused many serious environmental problems and how to ecologically recycle the inert solid waste has become a very challenging topic and attracts the attention from the scientists and policy makers.

However, coal refuse is relative inert solid wastes due to their major mineralogical compositions as stable aluminosilicate minerals at the ambient conditions, such as quartz, feldspar etc., which is hard toutilize as cementitious material for its lack of pozzolanic properties. Previous studieshave been conducted on the cementitious material composed of thermal activated coal refuse as pozzolanic material. N. Zhang et al. have successfully recycled red mud and coal refuse into cementitious material by thermal activation at 600°C (Zhang et al., 2011a, 2011b), and J. Zhang has demonstrated that coal refuse contains good pozzolanic properties after thermal activation(Zhang et al., 2010a, 2010b, 2010c). Other scientists tried to use integrated thermal and chemical activation to increase the pozzolanic properties of the coal refuse (Yu et al., 2006; Li et al., 2006; Yi et al., 2009; Chen et al., 2006). In this paper, a systematic study isconducted on evaluating the pozzolanic property of a coal refuse based cementitious material, which contains 25% coal refuse based pozzolana in cementitious material by activated at different temperature and time duration.

2. Material and Methods

2.1 Raw Material

The raw material used in this experiment includes coal refuse and US type I/II cement. The coal refuse was generated by a mining operation situated within the Central Appalachian Coal Basin in southwest Virginia, eastern Kentucky and southern West Virginia. The coal seams located near these operation sites were deposited during the Pennsylvania period and are located in the Pottsville Group from Pocahontas through the lower portions of the Allegheny formation. The chemical analysis was performed using an X-ray fluorescence (XRF-1700) analyzer, and mineral composition was detected by X-ray diffraction (XRD) with the Rigaku Ultimate.

2.2 Activation Procedure

Raw coal refuse is rock like irregular particles, therefore, it is necessary to crush and mill raw coal refuse into fine power coal refuse for cementitious material utilization. Coal refuse was crushed and then followed by grounding in a laboratory ball mill (50kg capacity) for 45min. Then the milled coal refuse was put inside of the furnace (Lindberg Blue M, Thermo Scientific) forthermal activationat different condition. The activation temperature (600°C-800°C) and time (0.5h-1.5h) were controlled as two significant parameters during the whole process to evaluate the pozzolanic property of the activated coal refuse. After the thermal activation process, the resultingsamples were removed from the furnace and allowed to cool spontaneously to room temperature in air. They were crushed in the laboratory ball mill to the Blaine's specific surface area of 601 m^2/kg.

2.3 Mortar Test

The compositions of different groups tested are listed in Table 1. It was important to use the same standard mixing method for the high-performance mortar tests, and all mortar samples were mixed according to ASTM C305 (Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency) and ASTM C109 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars) (ASTM C305, 2008; ASTM C109, 2008). The procedures were performed as described in the standard: all of the mixing water was placed into the bowl; cement was added to the water and the mixer was started at a low speed (140±5 r/min) for 30 seconds; aggregate was then added over a 30-second period while mixing at a low speed; and mixing was then increased to a medium speed (285±10 r/min) for 30 seconds of mixing. The mixer was stopped for 90 seconds to scrape down all of the mortar paste followed by mixing for 90 seconds at medium speed. Finally, the mixer was stopped, and mortar was cast into the mold. Cubic specimens (50 mm × 50 mm × 50 mm) were cast for each mixture for the unconfined compressive strength test (ASTM C109, 2008). Compression tests were performed on various specimens at seven curing ages (3, 7, 28Days). The test cubes were cured in a moist cabinet at 95% humidity and 23°C.

Table 1. Chemical, physical and mineral analysis of raw material

	Coal refuse	Cement
Al_2O_3(%)	13.89	2.78
SiO_2(%)	47.43	13.99
CaO(%)	4.55	62.11
Fe_2O_3(%)	11.19	3.34
SO_3(%)	0.27	2.54
K_2O(%)	3.24	0.29
MnO_2(%)	0.16	0.13
TiO_2(%)	1.02	0.10
Specific gravity (t/m^3)	2.70	3.11
Specific surface(m^2/kg)	601	445
Loss of ignite (%)	9.88	2.67
Major mineral component	Quartz Chloride Muscovite Kaolinite	LarniteHatruriteBrownmillerite

2.4 XRD and SEM Results

The target samples were prepared for observation using an XL30 FEG scanning electron microscope (SEM) with energy-dispersive X-ray microanalyses.

3. Experimental Results and Discussion

3.1 Pozzolanic Properties of Coal Refuse

In this test, the compressive strength test was used to evaluate the pozzolanic properties of the coal refuse based on cementitious material. As in Table 2, according to recipe of coal refuse based cementitious material (CR), the coal refuse activated at different condition and were mixed respectively to form different cementitious material groups. And the compressive strength results are presented in Figures 1, 2 and 3. From Figure 1, it is clearly seen that the 3 day strength of all coal refuse based cementitious material reaches more than 27 MPa. The 3 days strength of samples activated at 700°C and 800°C is higher than 28 MPa which is slightly better than that of ordinary Portland cement (OPC) group. When compared with the groups activated at different temperature, it is found that the groups with 1 h and 1.5h activation show better pozzolanic property than the group with 0.5h activation. As for the 7 and 28 day strength performance, it is also found the similar patternwhich shows that the 7 day strength of group activated at 700°C for 1 h reaches to 36.8 MPa, and it is higher than other groups in the 7 day strength test. In the 28 Day strength test, the strength of groups with 700°C 1h activation and 800°C 1h activation reaches 43.4MPa and 43.1 MPa respectively, which is higher than the 40MPa strength of OPC at 28 days. From these three sets of strengthtests at different curing age, it can be concluded that the activation temperature from 700°C to 800°C usually shows better activation performance than the activation at 500°C to 600°C when the process was conducted at the same time duration. And as for the same temperature activation condition, 1 h and 1.5 h activation shows better effect than activation within 0.5 h. However, when the economy and energy input consideration was input for an optimal solution, it can be referred that the activation at 700°C within 1h should be the practical answer.

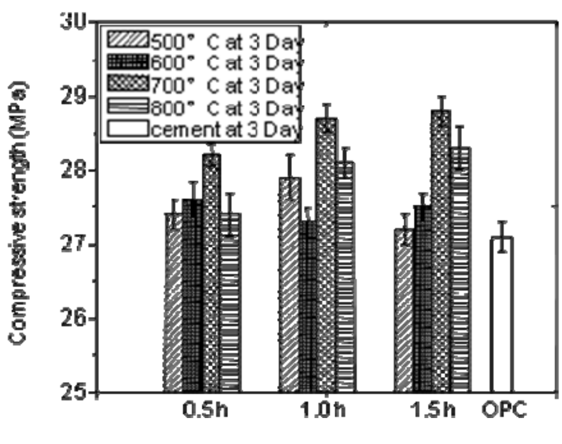

Figure 1. Compressive strength test at 3 Day

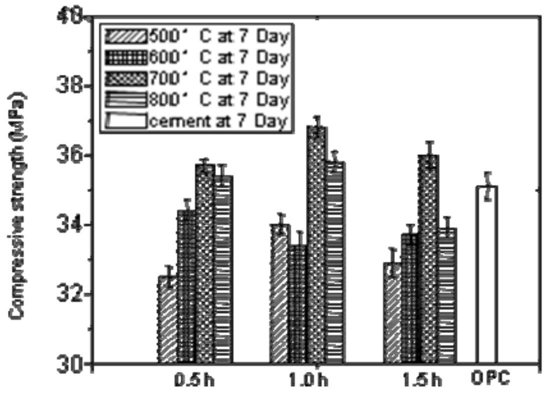

Figure 2. Compressive strength test at 7 Day

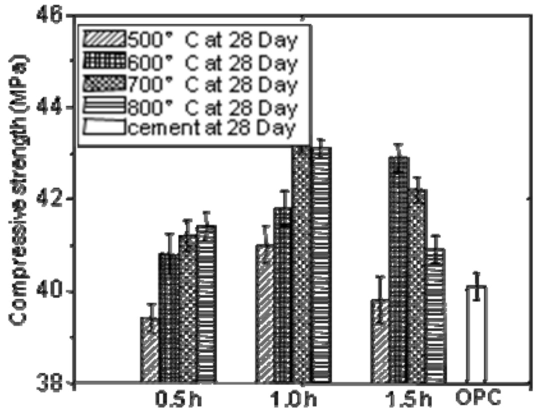

Figure 3. Compressive strength test at 28 Day

Table 2. Compositions of different tested groups

Sample	Cementitious materials (C) kg/m^3		Sand (S) kg/m^3	Water(W) kg/m^3	W/C	S/C
	Cement	Pozzolana				
OPC	500	0	1375	242	0.485	2.75
CR	375	125	1375	242	0.485	2.75

Pozzolana= Coal refuse + Gypsum (Coal refuse: Gypsum=20:1)

3.2 SEM Analysis

SEM was conducted on four 1 h activated samples (from 500°C to 800°C), the SEM images in Figures 4 to 7 illustrates the morphological characteristics of thermal-activated coal refuse. As shown from Figures 4 and 5, the coal refuse activated from 500°C to 600°C within 1 h shows the "scale-shaped" layered structure; however, as shown in Figures 6 and 7, this structure was destroyed when the temperature reached higher than 600°C. This might be due to the decomposition of minerals such as chlorite, muscovite, and kaolinite, which caused todestroy the layered structure. It is reported that kaolinite and muscovite disappeared at 600°C to 800°C (Zhang et al., 2011; Zhang et al., 2010). The kaolinite begins to decrease because of their transformation into metakaolin at 600°C to 800°C. And some previous study shows that the muscovite amorphizes at high temperature and high pressure (Zanazzi et al., 2002). Mazzucato et al has indicates that muscovite $2M_1$shows a major phase transition in coal refuse at about 800°C and the reaction taking in 700°C to 1000°C is truly a dehydroxylation process, involving the muscovite $2M_1$ gradually dehydroxylated to muscovite HT (Mazzucato et al., 1999). The generated amorphous materialsfrom parts of inert aluminosilicate minerals might be contribute to the improved pozzolanic properties. And this finds well agrees with morphological changes on thermal activation of coal waste (Zhang et al., 2011; Zhang et al., 2010).

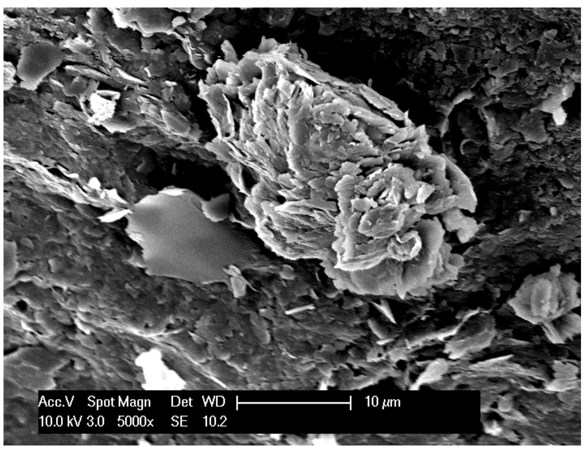

Figure 4. SEM of coal refuse activated at 500°C for 1hour

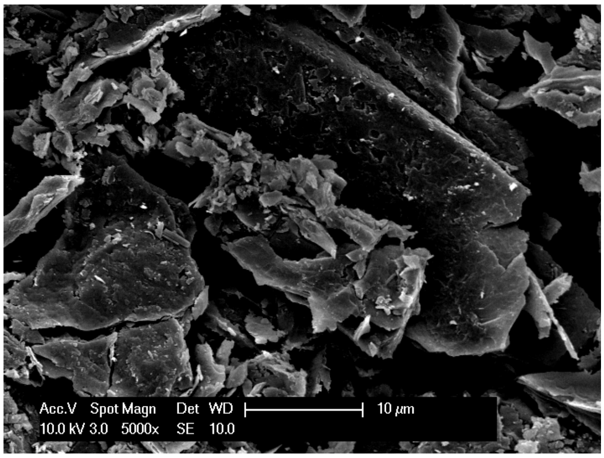

Figure 5. SEM of coal refuse activated at 600°C for 1hour

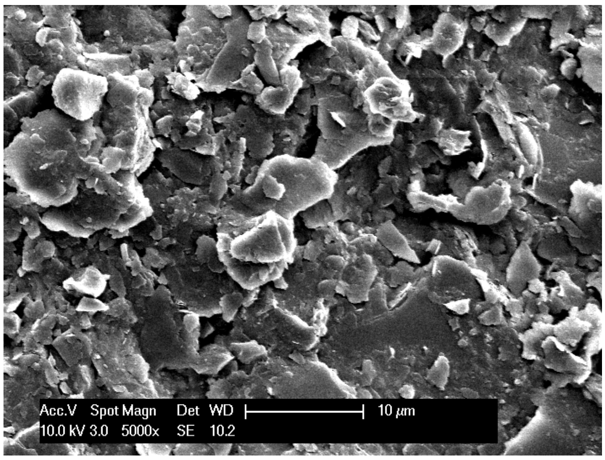

Figure 6. SEM of coal refuse activated at 700°C for 1hour

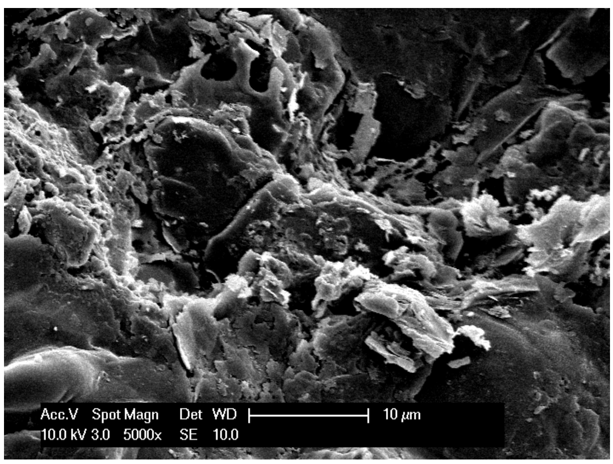

Figure 7. SEM of coal refuse activated at 800°C for 1hour

4. Conclusion

Coal refuse shows different pozzolanic properties when they were activated at different time and temperature. When the pozzolanic properties were investigated from 500°C to 800°C, it is found that coal refuse activated at 700°C to 800°C shows better pozzolanic property than that activated at 500°C to 600°C. And 1 hour activation shows better performance than the 0.5 h activation. Through the SEM image analysis, it is found that the coal refuse has layered scale microstructure at 500°C to 600°C, while this structure was destroyed when the temperature rise up to 700°C to 800°C. And this perhaps caused by the mineral phase change during the thermal activation.

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